

VERIFICATION OF TRANSLATION

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[Title of the Invention] APPARATUS AND METHOD FOR  
PRODUCING CARBON NANOFIBERS BY FLUIDIZING BED SYSTEM

[Claim(s)]

[Claim 1]

A method for producing carbon nanofibers, comprising:  
causing carbon nanofibers to grow on a surface of each  
of closely packed fine particles,  
recovering the closely packed fine particles and a  
closely packed fine particle on which the carbon nanofibers  
have grown, and  
separating the carbon nanofibers from the surface of  
the closely packed fine particle by a physical means to  
recover the carbon nanofibers.

[Claim 2]

A method for producing carbon nanofibers, comprising:  
causing carbon nanofibers to grow on a surface of each  
of closely packed fine particles,  
recovering the closely packed fine particles and a  
closely packed fine particle on which the carbon nanofibers  
have grown, and  
separating the carbon nanofibers from the surface of  
the closely packed fine particle by a chemical means to  
recover the carbon nanofibers.

[Claim 3]

The method according to claim 1 or 2, wherein when  
growth reaction for the carbon nanofibers is performed by  
either one of a gas flow layer reaction method, a fixed  
layer reaction method, a moving layer reaction method, and  
a fluidizing bed reaction method.

[Claim 4]

The method according to claim 3, wherein when the  
growth reaction for the carbon nanofibers is by the  
fluidizing bed reaction method, the closely packed fine

particle is utilized as a fluidizing material, the carbon nanofibers are caused to grow on the surface of the closely packed fine particle, and the carbon nanofibers are separated by collision among the closely packed fine particles in order to recover the carbon nanofibers, the collision taking place at the same time as the carbon nanofibers grow.

[Claim 5]

The method according to claim 3, wherein when the growth reaction for the carbon nanofibers is by the fluidizing bed reaction method, for causing the carbon nanofibers to grow on the surface of the closely packed fine particle utilizing the closely packed fine particle as a fluidizing material, a slow fluidizing state is created and the closely packed fine particles are vigorously stirred after reaction ends to separate the carbon nanofibers by collision among the closely packed fine particles in order to recover the carbon nanofibers.

[Claim 6]

The method according to any one of claims 1 to 5, wherein the closely packed fine particle is a high strength fine particle having low porosity.

[Claim 7]

The method according to claim 6, wherein a void ratio of the closely packed fine particle is 10% or less.

[Claim 8]

The method according to claim 6 or 7, wherein the closely packed fine particle includes one kind of or a mixture of two or more kinds of aluminum oxide, zirconium oxide, silicon carbide, and silicon nitride, or one kind of the compounds thereof as a main component and the content of the main component is 50 weight % or more.

[Claim 9]

The method according to any one of claims 1 to 8, wherein the closely packed fine particle from which the carbon nanofibers have been separated is recycled for reaction.

[Claim 10]

The method according to any one of claims 1 to 9, wherein a catalyst component is adhered to the closely packed fine particle.

[Claim 11]

The method according to claim 10, wherein the catalyst component is metal of one kind of or a combination of two or more kinds of Na, K, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Mo, W, Ru, Rh, Pd, Ir, Pt or a lanthanoid element such as La, Ce or Pr, and oxide thereof, chloride thereof, or nitrate thereof.

[Claim 12]

The method according to claim 11, wherein the catalyst contains an S component.

[Claim 13]

The method according to any one of claims 10 to 12, wherein an additive particle for peeling off the carbon nanofibers, which is different from the catalyst in particle shape, size, and material, is used to separate the carbon nanofibers.

[Claim 14]

The method according to any one of claims 1 to 5, wherein growth of the carbon nanofibers is divided into more than one growth.

[Claim 15]

The method according to any one of claims 1 to 5, wherein the carbon nanofibers are obtained by washing the carbon nanofibers that are peeled off from the closely packed fine particle with an acid solution, adding and

mixing an additive having a functional group with high affinity for a carbon nanofiber or with one end having a lipophilic functional group and an organic compound which is liquid at normal temperatures to the acid solution in which produced carbon nanofibers are dissolved, dispersing the carbon nanofibers in an organic compound solution, and vaporizing the organic compound solution in which the carbon nanofibers are dispersed.

[Claim 16]

The method according to claim 15, wherein the additive is a compound having a polynuclear aromatic functional group.

[Claim 17]

The method according to claim 16, wherein the compound having the polynuclear aromatic functional group is either one of anthracene, pyrene, and chrysene, or a mixture thereof.

[Claim 18]

The method according to claim 15, wherein the organic compound that is liquid at normal temperatures is normal hexane or toluene.

[Claim 19]

An apparatus for producing carbon nanofibers comprising:

a reaction means that supplies a carbon raw material and closely packed fine particles to cause carbon nanofibers to grow on a surface of each of the closely packed fine particles;

a heating means that heats the reaction means;

a recovery line that recovers a closely packed fine particle on which the carbon nanofibers have grown from the reaction means; and

a carbon nanofiber separating means that separates the

carbon nanofibers from the recovered closely packed fine particle on which the carbon nanofibers have been grown.

[Claim 20]

The apparatus according to claim 19, wherein the reaction means is one of a gas flow layer reaction means, a fixed layer reaction means, a moving layer reaction means, and a fluidizing bed reaction means.

[Claim 21]

The apparatus according to claim 19 or 20, wherein a catalyst supplying means that supplies a catalyst to the reaction means is provided.

[Claim 22]

The apparatus according to claim 21, wherein the catalyst supplying means is a liquid state supplying means that supplies the catalyst dissolved in the carbon raw material into the reaction means in a liquid state.

[Claim 23]

The apparatus according to claim 22, wherein the catalyst supplying means supplies the catalyst into the reaction means in a solid state or a gaseous state.

[Claim 24]

The apparatus according to claim 23, wherein the catalyst supplying means supplies the closely packed fine particle that carries the catalyst on the surface thereof into the reaction means.

[Claim 25]

The apparatus according to claim 24, wherein a catalyst carrying means that carries the catalyst on the surface of the closely packed fine particle is provided with a closely packed fine particle supplying means that supplies the closely packed fine particle into a carrying vessel main body and a spraying means that sprays the catalyst to the closely packed fine particle supplied to

the carrying vessel main body.

[Claim 26]

The apparatus according to claim 25, wherein the carrying vessel main body is of a fluidizing bed type and has a gas supplying means that supplies fluidizing gas.

[Claim 27]

The apparatus according to claim 25, wherein the carrying vessel main body is of a kiln type and has a rotary drum.

[Claim 28]

The apparatus according to any one of claims 19 to 27, wherein an average particle diameter of the closely packed fine particles is 0.2 to 20 mm.

[Claim 29]

The apparatus according to any one of claims 19 to 28, wherein the closely packed fine particle is a high strength fine particle having low porosity.

[Claim 30]

The apparatus according to any one of claims 19 to 29, wherein a void ratio of the closely packed fine particle is 10% or less.

[Claim 31]

The apparatus according to any one of claims 19 to 30, wherein the closely packed fine particle is one kind of or a mixture of two or more kinds of aluminum oxide, zirconium oxide, silicon carbide, and silicon nitride.

[Claim 32]

The apparatus according to any one of claims 19 to 31, wherein a reaction temperature by contacting between the catalyst and the carbon raw material is in a temperature range of 300°C to 1300°C and a pressure is 0.01 MPa or more.

[Claim 33]

The apparatus according to claim 19, wherein a

collision unit that collides against the closely packed fine particle is provided in the reaction means.

[Claim 34]

The apparatus according to claim 33, wherein the collision unit also functions as a heat transfer tube for adjusting the temperature in a reaction layer.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an apparatus and a method for producing carbon nanofibers using a fluidizing bed system.

[0002]

[Background Art]

A carbon nanotube is a tubular carbon polyhedron in which a graphite sheet is a closed cylindrical structure. The carbon nanotube comprises a multi-layer nanotube having a multi-layer structure where a graphite sheet is a closed cylindrical structure and a single-layer nanotube having a single layer structure where a graphite sheet is a closed cylindrical structure.

[0003]

The multi-layer nanotube, which is one of the types, was discovered by Iijima in 1991. That is, it was discovered that multi-layer nanotubes were present in a carbon mass deposited on a cathode in an arc discharge process (Nonpatent literature 1). Thereafter, research on multi-layer nanotubes has been actively conducted. In recent years, the research has reached such a level that multi-layer nanotubes can be synthesized in large quantities.

[0004]

By contrast, a single-layer nanotube has an inner

diameter of about 0.4 to 100 nanometers (nm), and the synthesizing thereof was simultaneously reported by Iijima and a group at IBM in 1993. The electronic state of a single-layer nanotube is theoretically predicted. It is considered that the electronic properties vary between being metallic and semi-conductive, depending on how the helix is wound. Accordingly, single-layer nanotubes are promising as a future electronic material.

[0005]

Other applications of single-layer nanotubes being considered include nanoelectronic materials, field electron emitters, highly directional radiation sources, soft X-ray sources, one-dimensional conductive materials, high heat conductive materials, hydrogen occluding materials, and the like. Further, it is thought that the application of single-layer nanotubes will be further expanded due to functional grouping of the surface, metal coating, and enclosing foreign material.

[0006]

Conventionally, the above-stated single-layer nanotubes are produced by introducing a metal such as iron, cobalt, nickel or lanthanum into an anodic carbon rod and performing arc discharge (Patent Literature 1).

However, when using this production method, in addition to producing single-layer nanotubes, multi-layer nanotubes, graphite, and amorphous carbon are mixed in the product; therefore, the yield is low and, in addition, yarn diameter and yarn length of the single-layer nanotubes fluctuate, resulting in that producing a high yield of single-layer nanotubes with relatively equal yarn diameters and yarn lengths is difficult.

[0007]

Besides the arc discharge method, additional methods

for producing carbon nanotubes have been proposed, which include a vapor-phase pyrolysis method, a laser sublimation method, an electrolytic method of a condensed phase, and the like (Patent documents 2 to 4).

[0008]

[Nonpatent literature 1]

S, Iijima, Nature, 354, 56 (1991)

[Patent document 1]

Japanese Patent Applications Laid-open No. H06-280116

[Patent document 2]

Japanese Patent No. 3100962

[Patent document 3]

Japanese Translation Publication (of PCT International Publication) No. 2001-520615

[Patent document 4]

Japanese Patent Applications Laid-open No. 2001-139317

[0009]

[Problem to be Solved by the Invention]

The respective production methods disclosed in these publications are directed to production methods performed in a laboratory or on a small scale and have a particular problem in that the yield of carbon material is low.

[0010]

Furthermore, when using the methods described above, stable mass production is difficult; for example, continuous production is unfeasible.

[0011]

On the other hand, for a nanosized carbon material (known as a carbon nanofiber) recently, usefulness thereof is expected in various fields, and feasibility of the industrial mass production is being desired.

[0012]

In the case of production using a fluidizing bed

furnace, when carbon nanofibers are separated from carbon nanofibers that have grown on a porous fluidizing material such as alumina, part of the fluidizing material is removed with the carbon nanofibers and efficiently separating the carbon nanofibers alone is difficult; therefore, improvement of the yield is desired.

[0013]

There is a problem in that the carbon nanofibers which have grown inside of the porous need to be refined and the refining takes labor and time, resulting in a rise in production cost of the carbon nanofibers.

[0014]

In view of the above circumstances, the problem to be solved by the present invention is to provide an apparatus and a method for enabling the continuous mass production of carbon nanofibers as a nanosized carbon material and improving the yield.

[0015]

[Means for Solving Problem]

A first invention for solving the above problem is a method for producing carbon nanofibers characterized by causing carbon nanofibers to grow on a surface of each of closely packed fine particles, recovering the closely packed fine particles and a closely packed fine particle on which the carbon nanofibers have grown, and separating the carbon nanofibers from the surface of the closely packed fine particle by a physical means to recover the carbon nanofibers.

[0016]

A second invention is a method for producing carbon nanofibers characterized by causing carbon nanofibers to grow on a surface of each of closely packed fine particles, recovering the closely packed fine particles and a closely

packed fine particle on which the carbon nanofibers have grown, and separating the carbon nanofibers from the surface of the closely packed fine particle by a chemical means to recover the carbon nanofibers.

[0017]

A third invention is the method for producing carbon nanofibers in the first or the second invention characterized in that growth reaction for the carbon nanofibers is performed by either one of a gas flow layer reaction method, a fixed layer reaction method and a moving layer reaction method and a fluidizing bed reaction method.

[0018]

A fourth invention is the method for producing carbon nanofibers in the third invention, characterized in that when the growth reaction for the carbon nanofibers is by the fluidizing bed reaction method, the closely packed fine particle is utilized as a fluidizing material, the carbon nanofibers are caused to grow on the surface of the closely packed fine particle, and the carbon nanofibers are separated by collision among the closely packed fine particles in order to recover the carbon nanofibers, the collision taking place at the same time as the carbon nanofibers grow.

[0019]

A fifth invention is the method for producing carbon nanofibers in the third invention, characterized in that, when the growth reaction for the carbon nanofibers is by the fluidizing bed reaction method, for causing the carbon nanofibers to grow on the surface of the closely packed fine particle utilizing the closely packed fine particle as a fluidizing material, a slow fluidizing state is created and the closely packed fine particles are vigorously stirred after reaction ends to separate the carbon

nanofibers by collision among the closely packed fine particles in order to recover the carbon nanofibers.

[0020]

A sixth invention is the method for producing carbon nanofibers in any one of the first to the fifth inventions, characterized in that the closely packed fine particle is a high strength fine particle having low porosity.

[0021]

A seventh invention is the method for producing carbon nanofibers in the sixth invention, characterized in that a void ratio of the closely packed fine particle is 10% or less.

[0022]

An eighth invention is the method for producing carbon nanofibers in the sixth or the seventh invention, characterized in that the closely packed fine particle includes one kind of or a mixture of two or more kinds of aluminum oxide, zirconium oxide, silicon carbide, and silicon nitride, or one kind of the compounds thereof as a main component and the content of the main component is 50 weight % or more.

[0023]

A ninth invention is the method for producing carbon nanofibers in any one of the first to the eighth inventions, characterized in that the closely packed fine particle from which the carbon nanofibers have been separated is recycled for reaction.

[0024]

A 10th invention is the method for producing carbon nanofibers in any one of the first to the ninth inventions, characterized in that a catalyst component is adhered to the closely packed fine particle.

[0025]

An 11th invention is the method for producing carbon nanofibers in the 10th invention, characterized in that the catalyst component is metal of one kind of or a combination of two or more kinds of Na, K, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Mo, W, Ru, Rh, Pd, Ir, Pt or a lanthanoid element such as La, Ce or Pr, and oxide thereof, chloride thereof, or nitrate thereof.

[0026]

A 12th invention is the method for producing carbon nanofibers in the 11th invention, characterized in that the catalyst contains an S component.

[0027]

A 13th invention is the method for producing carbon nanofibers in any one of the 10th to the 12th inventions, characterized in that an additive particle for peeling off the carbon nanofibers, which is different from the catalyst in particle shape, size, and material, is used to separate the carbon nanofibers.

[0028]

A 14th invention is the method for producing carbon nanofibers in any one of the first to the fifth inventions, characterized in that the growth of the carbon nanofibers is divided into more than one growth.

[0029]

A 15th invention is the method for producing carbon nanofibers in any one of the first to the fifth inventions, characterized in that the carbon nanofibers are obtained by washing the carbon nanofibers that are peeled off from the closely packed fine particle with an acid solution, adding and mixing an additive having a functional group with high affinity for a carbon nanofiber or with one end having a lipophilic functional group and an organic compound which is liquid at normal temperatures to the acid solution in

which produced carbon nanofibers are dissolved, dispersing the carbon nanofibers in an organic compound solution, and vaporizing the organic compound solution in which the carbon nanofibers are dispersed.

[0030]

A 16th invention is the method for producing carbon nanofibers in the 15th invention, characterized in that the additive is a compound having a polynuclear aromatic functional group.

[0031]

A 17th invention is the method for producing carbon nanofibers in the 16th invention, characterized in that the compound having the polynuclear aromatic functional group is either one of anthracene, pyrene, and chrysene, or a mixture thereof.

[0032]

A 18th invention is the method for producing carbon nanofibers in the 15th invention, characterized in that the organic compound that is liquid at normal temperatures is normal hexane or toluene.

[0033]

A 19th invention is an apparatus for producing carbon nanofibers characterized by including a reaction means that supplies a carbon raw material and closely packed fine particles to cause carbon nanofibers to grow on a surface of each of the closely packed fine particles, a heating means that heats the reaction means, a recovery line that recovers a closely packed fine particle on which the carbon nanofibers have grown from the reaction means, and a carbon nanofiber separating means that separates the carbon nanofibers from the recovered closely packed fine particle on which the carbon nanofibers have been grown.

[0034]

A 20th invention is the apparatus for producing carbon nanofibers in the 19th invention, characterized in that the reaction means is one of a gas flow layer reaction means, a fixed layer reaction means, a moving layer reaction means, and a fluidizing bed reaction means.

[0035]

A 21st invention is the apparatus for producing carbon nanofibers in the 19th or the 20th invention, characterized in that a catalyst supplying means that supplies a catalyst to the reaction means is provided.

[0036]

A 22nd invention is the apparatus for producing carbon nanofibers in the 21st invention, characterized in that the catalyst supplying means is a liquid state supplying means that supplies the catalyst dissolved in the carbon raw material into the reaction means in a liquid state.

[0037]

A 23rd invention is the apparatus for producing carbon nanofibers in the 22nd invention, characterized in that the catalyst supplying means supplies the catalyst into the reaction means in a solid state or a gaseous state.

[0038]

A 24th invention is the apparatus for producing carbon nanofibers in the 23rd invention, characterized in that the catalyst supplying means supplies the closely packed fine particle that carries the catalyst on the surface thereof into the reaction means.

[0039]

A 25th invention is the apparatus for producing carbon nanofibers in the 24th invention, characterized in that a catalyst carrying means that carries the catalyst on the surface of the closely packed fine particle is provided with a closely packed fine particle supplying means that

supplies the closely packed fine particle into a carrying vessel main body and a spraying means that sprays the catalyst to the closely packed fine particle supplied to the carrying vessel main body.

[0040]

A 26th invention is the apparatus for producing carbon nanofibers in the 25th invention, characterized in that the carrying vessel main body is of a fluidizing bed type and has a gas supplying means that supplies fluidizing gas.

[0041]

A 27th invention is the apparatus for producing carbon nanofibers in the 25th invention, characterized in that the carrying vessel main body is of a kiln type and has a rotary drum.

[0042]

A 28th invention is the apparatus for producing carbon nanofibers in any one of the 19th to the 27th inventions, characterized in that an average particle diameter of the closely packed fine particles is 0.2 to 20 mm.

[0043]

A 29th invention is the apparatus for producing carbon nanofibers in any one of the 19th to the 28th inventions, characterized in that the closely packed fine particle is a high strength fine particle having low porosity.

[0044]

A 30th invention is the apparatus for producing carbon nanofibers in any one of the 19th to the 29th inventions, characterized in that a void ratio of the closely packed fine particle is 10% or less.

[0045]

A 31st invention is the apparatus for producing carbon nanofibers in any one of the 19th to the 30th inventions, characterized in that the closely packed fine particle is

one kind of or a mixture of two or more kinds of aluminum oxide, zirconium oxide, silicon carbide, and silicon nitride.

[0046]

A 32nd invention is the apparatus for producing carbon nanofibers in any one of the 19th to the 31st inventions, characterized in that a reaction temperature by contacting between the catalyst and the carbon raw material is in a temperature range of 300°C to 1300°C and a pressure is 0.01 MPa or more.

[0047]

A 33rd invention is the apparatus for producing carbon nanofibers in the 19th invention, characterized in that a collision unit that collides against the closely packed fine particle is provided in the reaction means.

[0048]

A 34th invention is the apparatus for producing carbon nanofibers in the 33rd invention, characterized in that the collision unit also functions as a heat transfer tube for adjusting the temperature in a reaction layer.

[0049]

[Embodiment of the Invention]

Embodiments of the present invention will be explained in detail below; provided, however, the present invention is not limited thereby.

[0050]

Figs. 1 are illustrative diagrams of states where carbon nanofibers grow on each of closely packed fine particles according to a present embodiment. Fig. 1(a) is a status diagram where catalysts 51 are carried on a surface of a closely packed fine particle 50. Fig. 1(b) is a status diagram where carbon nanofibers 52 grow by catalytic action. Fig. 1(c) is a status diagram where

carbon nanofibers are separated from the closely packed fine particle 50 by physical or chemical action. Fig. 1(d) is a status diagram where the catalysts 51 are dissolved by acid dissolution to obtain the carbon nanofibers.

[0051]

The method for producing carbon nanofibers according to the present invention is for causing the carbon nanofibers 52 to grow on a surface of the closely packed fine particles 50, recovering the closely packed fine particles 50 and the closely packed fine particle 50 on which the carbon nanofibers 52 have grown, separating the carbon nanofibers 52 from the surface of the closely packed fine particle 50 by a physical (or mechanical) means in order to recover the carbon nanofibers 52.

[0052]

The physical means can be, for example, using a ball mill 54 as shown in Fig. 2 and separating the carbon nanofibers 52 from a closely packed fine particle 55 on which carbon nanofibers have grown by mechanical surface friction occurring during rotation. As shown in Figs. 1, the carbon nanofibers 52 that have grown on the surface of the closely packed fine particle 50 like beards are represented by a black circle (reference numeral 55) for the convenience of explaining Fig. 2 (hereinafter, the same is applied).

[0053]

Use of catalyst is preferable for promoting growth of the carbon nanofibers. For example, metal of one kind of or a combination of two or more kinds of Na, K, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Mo, W, Ru, Rh, Pd, Ir, Pt or a lanthanoid element such as La, Ce or Pr, and oxide thereof, chloride thereof or nitrate thereof can be used.

[0054]

As alloy of the transition metal, for example, Co-Mo based catalyst metal components can be enumerated, however, the present invention is not limited thereto.

[0055]

Furthermore, for example, thiophene as an S component can be added to the catalyst as a growth accelerator for a carbon nanofiber. Here, adding the S component is based on the reason that it is considered to have neutralizing action for catalyst poisoning and properly contribute to activation of the catalyst.

[0056]

The catalyst 51 adhered onto the carbon nanofiber 52 may be removed by a catalyst removing method such as acid washing.

As another physical means except for the ball mill, for example, an ultrasonic vibrating means can be enumerated, which however is not limited thereto.

[0057]

In the present invention, the closely packed fine particle means a high strength fine particle having low porosity.

More specifically, the void ratio of the fine particle may be 10% or less, preferably 5% or less, further preferably 3 to 5%, inclusive, and more preferably 1 to 3%, inclusive. The lower void ratio allows preventing of peeling-off of the closely packed fine particle when separating a carbon nanofiber, thereby enabling the obtaining of a carbon nanofiber without the presence of the fine particle, which is an impurity.

[0058]

It is preferable that the closely packed fine particle includes one kind of or a mixture of two or more kinds of aluminum oxide, zirconium oxide, silicon carbide, and

silicon nitride, or one kind of the compounds thereof as a main component and the content of the main component is 50 weight % or more.

[0059]

The particle size of the closely packed fine particle is not limited in particular; however, the particle having a range of 0.02 to 20 mm can be employed.

[0060]

The hardness of the closely packed fine particle can be, for example, Moh's hardness of 5 or more, and preferably Moh's hardness of 8 or more (old Moh's hardness). By employing the above, when carbon nanofibers are separated, peeling-off of the surface of the fine particle is prevented, thereby enabling the isolation of the carbon nanofibers alone.

[0061]

According to the closely packed fine particle 50 as shown in Fig. 19(a), the carbon nanofibers 52 can grow only from the surface, so that separating the carbon nanofibers is facilitated.

[0062]

On the other hand, in case of using a porous fine particle 80 as shown in Fig. 19(b), when separating the carbon nanofibers 52, the carbon nanofibers 52 together with a surface of the porous fine particle are peeled off due to undulation of a porous surface, and the porous fine particle constitutes impurity, which results in low purity.

[0063]

Furthermore, when the catalysts 51 adhere also to inside of porous portions 81 in the porous particle 80 as shown in Fig. 19(c) and the carbon nanofibers 52 grow from the catalysts, the carbon nanofibers alone cannot be isolated, which necessitates dissolving the entire portion

(denoted by a dashed line in the figure) using an acid solution; and the dissolving work takes labor and time.

In particular, in case of a soft fine particle, a large amount of the fine particle would be peeled off at peeling-off, which results in an increase in an amount of impurities.

[0064]

As a consequence of the use of the closely packed fine particle with high strength having low porosity according to the present invention, wear of the closely packed fine particle itself is reduced and the amount of catalysts can be reduced.

Furthermore, separation is facilitated by wearing and impurity in a product is much reduced, thereby enabling the obtaining of a carbon nanofiber with high purity.

In this manner, according to the present invention, a carbon nanofiber with impurity of 5% or less can be obtained; however, the use of a conventional porous fine particle only allows obtaining a carbon nanofiber containing 40 to 70% impurities.

Furthermore, it is densified and the hardness is high, not allowing peeling off, whereby recycling is effective.

[0065]

Fig. 3 is an explanatory diagram of a chemical separating method. As shown in Fig. 3, the method for producing carbon nanofibers using the chemical separating process includes causing the carbon nanofibers 52 to grow on the surface of each of the closely packed fine particles 50, recovering the closely packed fine particles and the closely packed fine particle 55 on which the carbon nanofibers have grown, separating the carbon nanofibers 52 from the surface of the closely packed fine particle 50 by a chemical means using acid solution 56, and recovering the

carbon nanofibers 52.

[0066]

As shown in Fig. 4, the closely packed fine particle 50 from which the carbon nanofibers 52 have been separated is reusable for reaction. Some loss can be replenished by the closely packed fine particles 50.

[0067]

Furthermore, as shown in Fig. 5, adhesion of the catalysts 51 to the closely packed fine particle 50 may be performed by feeding the closely packed fine particles 50 into a catalyst carrying vessel 60 or supplying them using a fine particle supplying means, and spraying catalyst containing liquid 62 from a spraying means 63 in order to carry the catalysts 51 on the surface of the closely packed fine particle 50. The catalysts are efficiently adhered to the surface thereof by supplying fluidizing gas 64 into the catalyst carrying vessel 60 from the bottom and allowing the closely packed fine particles 50 to be in a fluidized state.

[0068]

As shown in Fig. 6, adhesion of the catalyst 51 can be performed by providing the spraying means 63 that sprays the catalyst containing liquid 62 inside a rotary kiln 66 while rotating the closely packed fine particles 50.

[0069]

As shown in Fig. 7, the carbon nanofibers 52 are caused to grow on the surface of each of the closely packed fine particles 50 through the catalysts 51, the closely packed fine particles and the closely packed fine particle 55 on which the carbon nanofibers have grown are recovered, the carbon nanofibers 52 are separated from the surface of the closely packed fine particle 50 by the chemical separating process using the acid solution 56, and the

carbon nanofibers 52 are recovered, for which catalytic solution 58 dissolved in the acid solution can be made recycled. Some loss can be replenished.

[0070]

The reaction method of carbon nanofibers is not limited in particular; for example, there enumerated a fluidizing bed system as shown in Fig. 8 for feeding the closely packed fine particles 50 as a fluidizing material into a fluidizing furnace 71 for fluidizing and feeding raw material gas 72 from the bottom to be extracted from the top in order to conduct reaction; a moving layer system as shown in Fig. 9 for filling the closely packed fine particles 50 into a moving bed furnace 73, gradually feeding the closely packed fine particles and extracting some thereof, and also injecting the raw material gas 72 from the bottom and extracting from the top to conduct reaction; a fixed bed system as shown in Fig. 10 for injecting the raw material gas 72 into a fixed bed furnace 74 from the bottom and extracting from the top to conduct reaction; and a gas flow bed system as shown in Fig. 11 for feeding the closely packed fine particles 50 with the raw material gas 72 from one end of a vapor phase reaction furnace 75 to conduct reaction and recover the reactant at another end.

At this time, catalysts can be pre-carried on the closely packed fine particle or catalysts can be fed separately, and the filling method of catalysts is not limited in particular.

[0071]

As shown in Fig. 12, the closely packed fine particles 50 to be supplied inside can be pre-heated in a preheating furnace 76, and then supplied to the vapor phase reaction furnace 75 having a heating means 77, thereby achieving

uniformity of the reaction temperature by heat capacity of the closely packed fine particles preheated and properly conducting reaction.

[0072]

Next, a specific example of an apparatus for producing carbon nanofibers is shown in Fig. 13. As shown in Fig. 1, the apparatus for producing carbon nanofibers is provided with a fluidizing bed reaction unit 12 filled with the closely packed fine particles 50, each of which carries the catalysts 51 which is a fluidizing material inside thereof, a raw material supplying means 14 that supplies a carbon raw material 13 which is raw material gas into the fluidizing bed reaction unit 12, a catalyst-carrying fine particle supplying means 16 that supplies the closely packed fine particles 50, each of which carries the catalysts 51 into the fluidizing bed reaction unit 12, a free board unit 17 having a space where the closely packed fine particles which are a fluidizing material in the fluidizing bed reaction unit 12 scatter or flow down, a fluidizing gas supplying means 19 that supplies fluidizing gas 18 which fluidizes the fluidizing material 11 inside, a heating means 20 that heats the fluidizing bed reaction unit 12, a recovery line 23 that recovers the carbon nanofibers 52 and the closely packed fine particles 50 scattered from the free board unit 17, a separating means 24 that separates the carbon nanofibers 52 from the closely packed fine particle 50 recovered in the recovery line 23, and a refining means 27 that removes the catalyst adhered to the carbon nanofiber 52.

[0073]

As a fluidizing bed reaction type of the fluidizing bed reaction unit 12, there are a bubble fluidizing bed type and a jet fluidizing bed type, and either one can be

used in the present invention.

In this embodiment, the fluidizing bed reaction unit 12 and the free board unit 17 constitute a fluidizing bed reactor 25.

Further, it is preferable that the free board unit 17 has a cross sectional area of a flow path larger than that of the fluidizing bed reaction unit 12.

[0074]

The carbon raw material 13 supplied from the carbon material supplying unit 14 may be any one of compounds containing carbon, for example, there enumerated CO and CO<sub>2</sub>, and in addition, alkanes such as methane, ethane, propane and hexane; unsaturated organic compound such as ethylene, propylene and acetylene; aromatic compound such as benzene and toluene; a polymer material such as polyethylene and polypropylene; or oil or coal (including coal converted gas), however the present invention is not limited thereto.

Furthermore, organic compound containing not only C or H component but also an S component or a Cl component may be used.

[0075]

The carbon raw material 13 is supplied to the fluidizing bed reaction unit 12 in a gaseous state and is subjected to a uniform reaction by stirring conducted by the closely packed fine particles 50 which are a fluidizing material, thereby causing carbon nanofibers to grow. At that time, inert gas is separately introduced as fluidizing gas from the fluidizing gas supplying means 19 into the fluidizing bed reaction unit 17.

[0076]

Supplying of the catalysts can be performed by pre-carrying catalysts on the surface of the closely packed fine particle and, in addition by dissolving the catalysts

51 in the carbon raw material 13 to be supplied into the reaction means in a liquid state. In this case, the catalyst-carrying fine particle supplying means 16 can simply serve as a supplying means for the closely packed fine particles 50 and the raw material supplying means 14 can serve as a means for supplying the catalysts in a liquid state.

[0077]

Furthermore, a catalyst may be supplied into the reaction means in a solid or gaseous state. In this case, a catalyst supplying means may be provided separately.

[0078]

Carbon fibers are synthesized by setting a temperature range of 300°C to 1300°C, and more preferably a temperature range of 400°C to 1200°C and causing carbon material such as benzene to contact with a catalyst for a fixed time in mixed gas with a hydrogen partial pressure of 0% to 90%.

[0079]

As the separating means 24, in addition to a cyclone, for example, a publicly known separating means such as a bug filter, a ceramic filter, and a sieve can be used.

[0080]

Moreover, the carbon nanofibers 22 separated by the separating means 24 are recovered as a pure product of the carbon nanofiber by the refining means 27 separating the adhered catalyst.

[0081]

Furthermore, by utilizing the closely packed fine particle as the fluidizing material, the carbon nanofibers are caused to grow on the surface of the closely packed fine particle, and the carbon nanofibers are separated by collision among the closely packed fine particles in order to recover the carbon nanofibers, the collision taking

place at the same time as the carbon nanofibers grow.

[0082]

As shown in Fig. 14, by providing a pressurizing unit 21 that pressurizes interior of the fluidizing bed reaction unit 12, a pressurizing condition can be achieved therein.

[0083]

As the pressurizing unit 21, for example, liquefied nitrogen can be enumerated; and the fluidizing material supplying means 26, the raw material supplying means 14, the fluidizing gas supplying means 19, and the catalyst-carrying particle supplying means 16 are pressurized by a pressure-adjusting valve 28 and a carburetor 29.

For the pressurizing condition, 0.01 MPa or more, preferably 0.5 MPa, and more preferably 2 MPa would be preferable. It is preferable that the upper limit is set to 3 MPa.

Setting 0.01 MPa or more results in a fast reaction speed, whereby the reaction efficiency can be improved. A deposition condition for carbon nanofibers can be controlled according to the pressurized condition.

In case of exceeding 3 MPa, a pressure-resistant reference for apparatuses and peripheral devices becomes high and manufacturing costs increase, which is not desirable.

[0084]

By setting the interior of the fluidizing bed reaction unit 12 to the pressurizing condition in this manner, the reaction efficiency can be improved.

[0085]

As shown in Fig. 15, different reaction conditions may be employed to create a slow fluidizing bed under a first reaction condition and a vigorous fluidizing bed under a second reaction condition by temporally varying the flow

rate of the fluidizing gas 18 supplied to the fluidizing bed reaction unit 12.

Thereby after the reaction has progressed for a fixed time by staying in a slow fluidizing bed, the closely packed fine particles are moved to the vigorous fluidizing bed, where the fine particles are vigorously stirred by the fluidizing gas 18 with a rapid flow rate to cause wear among the fine particles, whereby the carbon nanofibers 52 produced on the surface of each of the closely packed fine particles are separated and discharged externally as a product 32 together with the exhaust gas 33; thus, the carbon nanofibers may be recovered.

[0086]

As shown in Fig. 16, the interior of the fluidizing bed reaction unit 12 can be partitioned into two portions by a partition member 31 and reaction conditions are made different by varying the flow rate of the fluidizing gas 18 such that one portion is a slow fluidizing bed 12A and the other portion is a vigorous fluidizing bed 12B.

Thereby, after the reaction has progressed for a fixed time in the slow fluidizing bed 12A, the closely packed fine particles are moved to the vigorous fluidizing bed 12B, where the closely packed fine particles are vigorously stirred by the fluidizing gas 18 with a rapid flow rate to cause wearing among the fine particles, whereby the carbon nanofibers 52 produced on the surface of each of the closely packed fine particles are separated and discharged externally as the product 32 together with the exhaust gas 33; thus, the carbon nanofibers 52 may be recovered.

[0087]

Furthermore, as shown in Fig. 17, there can be provided partition plates 41A to 41H for pluralizing the interior of the fluidizing bed reaction unit 12 so as to

reduce the distribution of the staying time of the closely packed fine particles in each fluidizing bed.

[0088]

As shown in Fig. 18, a plurality of fluidizing bed reactors 25A to 25D can be provided and reacted particles are gradually extracted from the each fluidizing bed reaction unit 12 in order to reduce the distribution of the particle staying time. Extraction from the fluidizing bed reactor 25D is performed from the bottom of the furnace.

Furthermore, the product 32 and the exhaust gas 33 are individually recovered from the each fluidizing bed reactor and the carbon nanofibers are refined.

[0089]

Furthermore, as shown in Fig. 20, carbon nanofibers can be separated by feeding additive particles 91 for peeling off carbon nanofibers that are different in shape, size, and material from the catalysts, into the fluidizing bed reaction unit 12.

[0090]

For the additive particles 91 that peel off carbon nanofibers, the additive particles 91 can be employed that have a suitable combination of the following properties with respect to the catalyst: an identical shape but a different diameter, a different shape, a different material, and a different particle diameter.

[0091]

For example, when the shape of a catalyst particle is spherical, a cubic additive particle is preferable. With such a combination, when particles make contact with one another, local collision causes a large partial impact, which promotes peeling-off of the carbon nanofiber from the catalyst particle.

[0092]

For example, high strength ceramics can be employed as the closely packed fine particles and the additive particles 91 can be columnar and made from stainless steel. In the fluidizing bed reaction unit 12, the stainless-steel columnar additive particles 91 impact on carbon nanofibers to promote peeling-off. On the other hand, since the stainless-steel columnar additive particles 91 are softer than the high strength ceramics, the high strength ceramics do not wear; therefore, the life of high strength ceramics can be improved. Many thin stainless-steel pieces are included in particles scattered from the fluidizing bed and the number of thin pieces of the high strength ceramics is reduced, so that the carbon nanofiber concentration can be improved easily by acid processing of the scattered particles.

[0093]

By using magnetic material (for example, a cobalt-based alloy material) as the additive particle for peeling-off, the purity of carbon nanofibers can be improved by separation utilizing a magnetic force.

[0094]

Furthermore, additive particles having a particle diameter smaller than that of the closely packed fine particles can be used to form a fluidizing bed, closely packed fine particles on which catalysts are adhered can be supplied from an upper portion of the fluidizing bed, and carbon nanofibers can be caused to grow while large catalyst particles are being slowly settled in order to peel off the carbon nanofibers. The settling time can be controlled according to the difference in the particle diameter between the particles, thereby enabling the adjustment of the reaction time.

[0095]

An eddy flow is formed near the lower end of the fluidizing bed reaction unit 12, and when catalyst particles on which carbon nanofibers have grown settle, collisions among particles are promoted by the impact of the eddy flow, so that peeling-off of the carbon nanofibers is promoted. Fluidizing gas may be supplied in a tangential direction in order to form the eddy flow, and for example, an eddy flow perforated plate may be formed on a lower portion side of the fluidizing bed reaction unit 12.

[0096]

By feeding additive particles for peeling-off inside the reaction layer, wear can be promoted in the fluidizing bed reaction, and, by using additive particles made of stainless steel or the like and dissolved in acid at the time of separation, separation efficiency is increased, so that the impurity level of the carbon nanofibers can be improved. By changing the particle diameter appropriately, it becomes possible to control the staying time of the closely packed fine particle carrying catalysts inside the fluidizing bed, thereby enabling arbitrary control of the reaction time.

[0097]

By adopting a magnetic material for the additive particles, separation utilizing a magnetic force becomes possible after the recovery.

[0098]

As shown in Fig. 21, by arranging baffle plates 92, which are collision plates, in a direction perpendicular to the fluidization direction inside the fluidizing bed reaction unit 12, the number of collisions is increased during fluidization, whereby the peeling-off efficiency of carbon nanofibers is improved.

The baffle plate 92 may also function as a heat

transfer tube heating the interior.

[0099]

As shown in Fig. 22, a pure product of the carbon nanofibers 52 can be obtained by recovering the closely packed fine particles 55 on which carbon nanofibers have grown by the reaction to be washed with the acid solution 56, then adding organic compound solution 96 obtained by mixing additive 93 having a functional group with high affinity for a carbon nanofiber or with one end having a lipophilic functional group and organic compound 94 which is liquid at normal temperatures to the acid solution 56 in which the produced carbon nanofibers are dissolved, dispersing carbon nanofiber dispersions 95 enclosed by the additives 93 in the organic compound solution 96, subsequently removing the acid solution 56 and the closely packed fine particles 50 from which the carbon nanofibers have been peeled off, heating the organic compound solution containing the carbon nanofiber dispersions 95, separating the additives 93 which are micelle particles 97 constituted as an aggregation of the additives from the carbon nanofiber 52, and thereafter recovering the additives 93 and the organic solvent 94.

[0100]

As a functional group with satisfactory affinity for a carbon nanofiber, the compound having a polynuclear aromatic functional group is preferable.

[0101]

As a compound having the polynuclear aromatic functional group, either one of anthracene, pyrene, and chrysene, or a mixture thereof can be enumerated.

[0102]

Furthermore, as an organic compound which is liquid at normal temperatures, for example, normal hexane and toluene

can be enumerated.

[0103]

A carbon nanofiber can be isolated by using an additive whose affinity for an organic compound and a carbon nanofiber varies according to the temperature condition, whereby elevating the temperature deactivates the affinity between the additive and the carbon nanofiber and dissolves the additives 96 aggregated in the micelle state into the organic solvent 94. Thereafter, the organic solvent and the additives are vaporized and recovered. As a result, the carbon nanofibers can be isolated and the additives can also be recovered, whereby the additives can be recycled.

[0104]

[Effect of the Invention]

As described above, producing carbon nanofibers using the closely packed fine particles according to the present invention enables an efficient and high-yield production of carbon nanofibers with high purity, thereby allowing industrial mass production and low-cost production of carbon nanofibers.

[Brief Description of Drawings]

[FIG. 1] Illustrative diagrams of growth of carbon nanofibers according to an embodiment.

[FIG. 2] A schematic diagram of a physically separating step of the carbon nanofibers according to the embodiment.

[FIG. 3] A schematic diagram of a chemically separating step of the carbon nanofibers according to the embodiment.

[FIG. 4] A schematic diagram of a producing step of the carbon nanofibers according to the embodiment.

[FIG. 5] A schematic diagram of a producing step of adhering catalysts to a closely packed fine particle according to the embodiment.

[FIG. 6] A schematic diagram of another producing step of adhering catalysts to a closely packed fine particle according to the embodiment.

[FIG. 7] A schematic diagram of a step of reusing the catalysts carried on the closely packed fine particle according to the embodiment.

[FIG. 8] A schematic diagram of a fluidizing bed reaction system according to the embodiment.

[FIG. 9] A schematic diagram of a moving bed reaction system according to the embodiment.

[FIG. 10] A schematic diagram of a fixed bed reaction system according to the embodiment.

[FIG. 11] A schematic diagram of a gas flow bed reaction system according to the embodiment.

[FIG. 12] A schematic diagram of another gas flow bed reaction system according to the embodiment.

[FIG. 13] A schematic diagram of a fluidizing bed reaction system according to the embodiment.

[FIG. 14] A schematic diagram of another fluidizing bed reaction system according to the embodiment.

[FIG. 15] A schematic diagram of a fluidizing bed reaction system with different fluidizing conditions according to the embodiment.

[FIG. 16] A schematic diagram of another fluidizing bed reaction system with different fluidizing conditions according to the embodiment.

[FIG. 17] A schematic diagram of still another fluidizing bed reaction system with different fluidizing conditions according to the embodiment.

[FIG. 18] A schematic diagram of still another fluidizing bed reaction system with different fluidizing conditions according to the embodiment.

[FIG. 19] Illustrative diagrams showing states of peeling

the carbon nanofibers.

[FIG. 20] A schematic diagram of another fluidizing bed reactor according to the embodiment.

[FIG. 21] A schematic diagram of still another fluidizing bed reactor according to the embodiment.

[FIG. 22] A schematic diagram of still another fluidizing bed reactor according to the embodiment.

[Explanations of Letters or Numerals]

- 11 fluidizing material
- 12 fluidizing bed reaction unit
- 13 carbon material
- 14 raw material supplying means
- 15 catalytic metal
- 16 catalyst-carrying fine particle supplying means
- 17 free board unit
- 18 fluidizing gas
- 19 fluidizing gas supplying means
- 20 heating means
- 23 recovery line
- 24 separating means
- 50 closely packed fine particle
- 51 catalyst
- 52 carbon nanofiber
- 54 ball mill
- 55 closely packed fine particle on which carbon nanofibers have grown
- 56 acid solution

[Type of Document] Abstract

[Abstract]

[Problem to be solved]

To provide an apparatus and a method for producing a carbon nanofiber which is a nanosized carbon material and which can be continuously mass-produced with an improved yield.

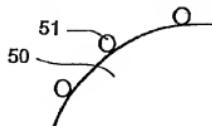
[Solution]

Carbon nanofibers 52 are recovered by causing the carbon nanofibers 52 to grow on a surface of each of closely packed fine particles 50, recovering the closely packed fine particles 50 and the closely packed fine particle 50 on which the carbon nanofibers 52 have grown, and separating the carbon nanofibers 52 from the surface of the closely packed fine particle 50 by a physical means. This enables an efficient and high-yield production of carbon nanofibers with high purity, thereby allowing industrial mass production and low-cost production of the carbon nanofibers.

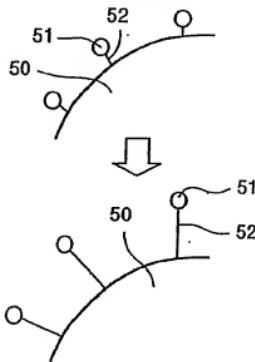
[Chosen Drawing] FIG. 1

# FIG.1

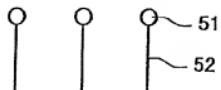
(a) CARRY CATALYSTS ON CLOSELY PACKED FINE PARTICLE



(b) CARBON NANOFIBERS GROW BY CATALYTIC ACTION

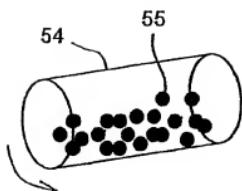


(c) SEPARATE CARBON NANOFIBERS FROM CLOSELY PACKED FINE PARTICLE BY PHYSICAL OR CHEMICAL ACTION

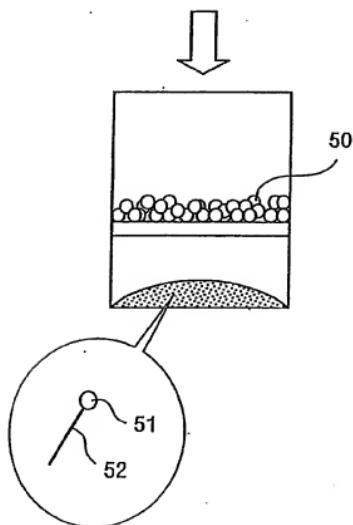


(d) DISSOLVE CATALYSTS BY ACID DISSOLUTION



**FIG.2**

MECHANICAL SURFACE FRICTION BY SUCH AS BALL MILL



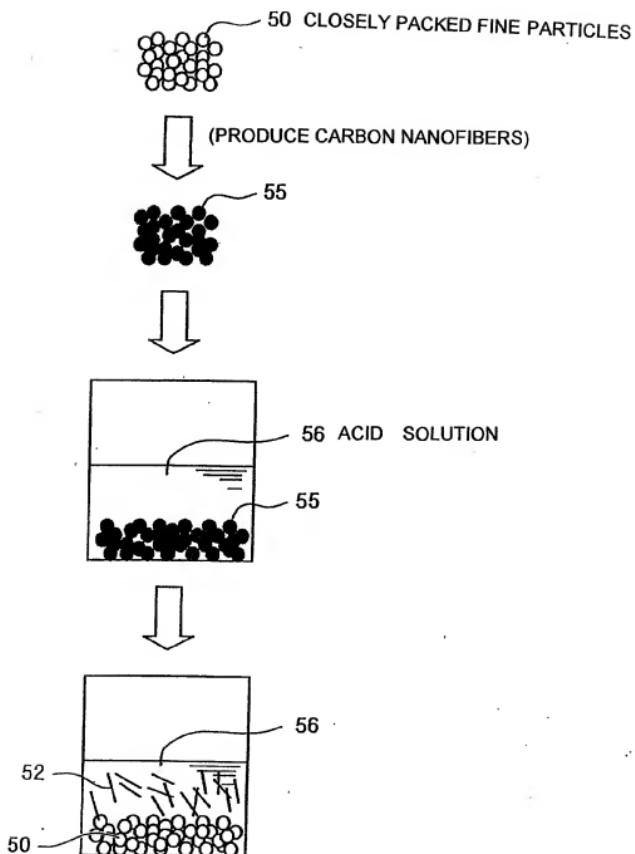
**FIG.3**

FIG.4

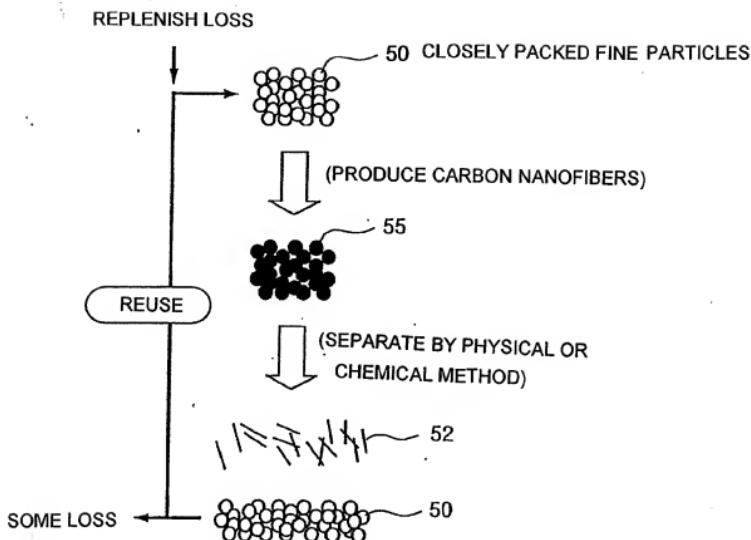
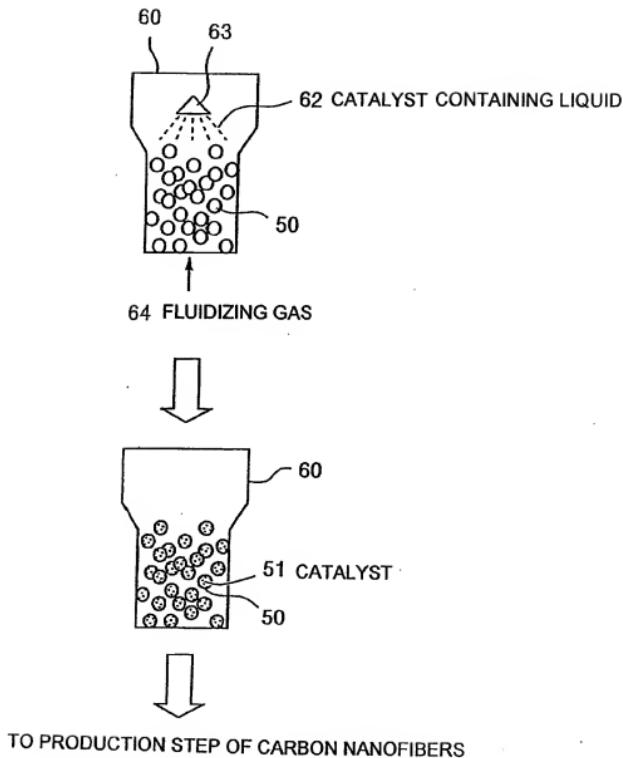


FIG.5



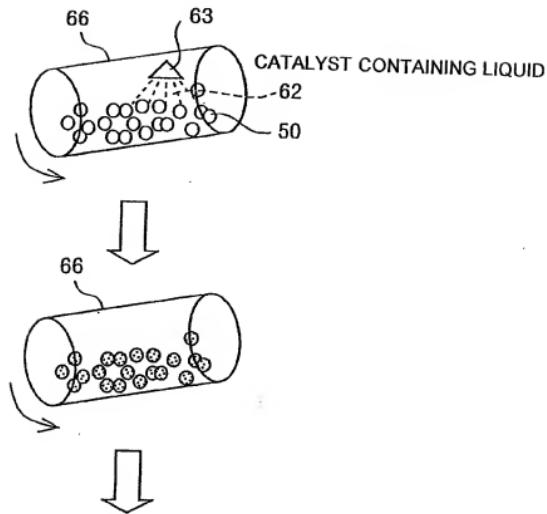
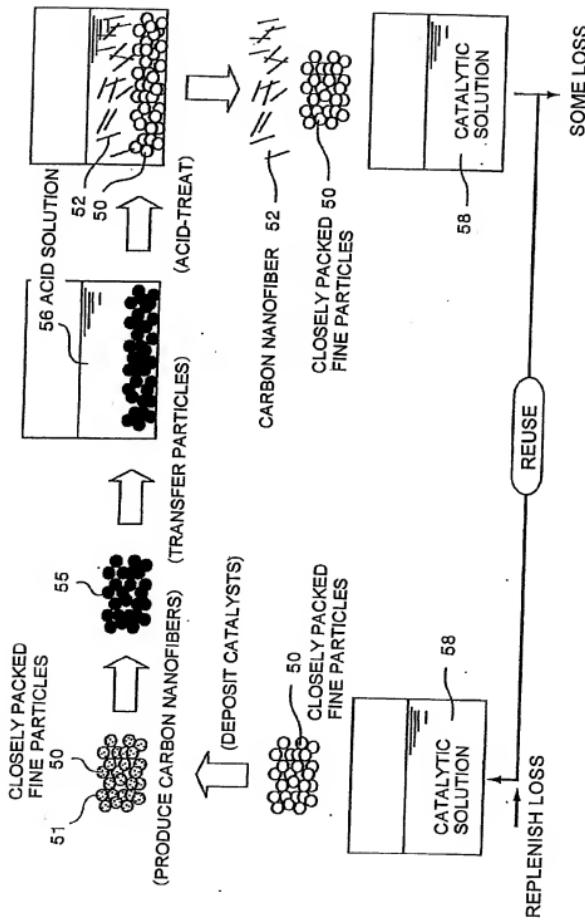
**FIG.6**

FIG. 7



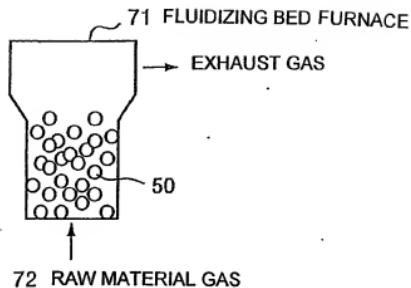
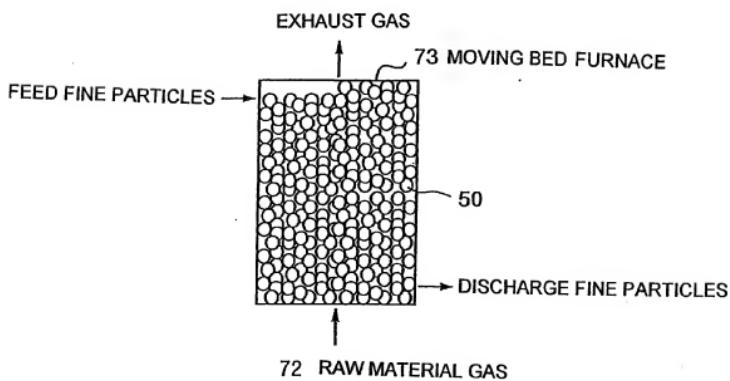
**FIG.8****FIG.9**

FIG.10

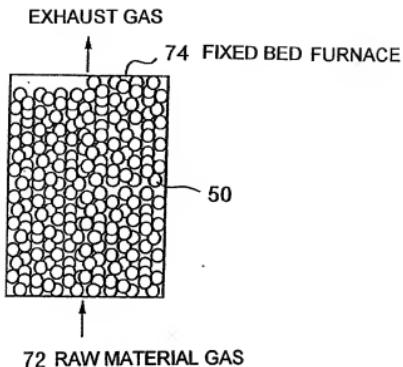


FIG.11

72 RAW MATERIAL GAS

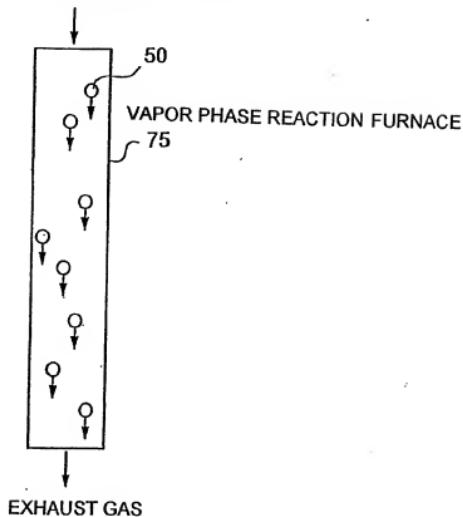


FIG.12

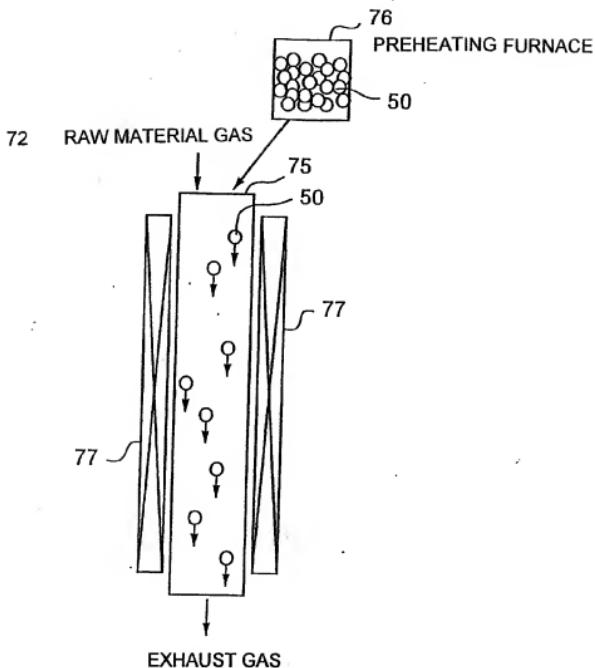


FIG.13

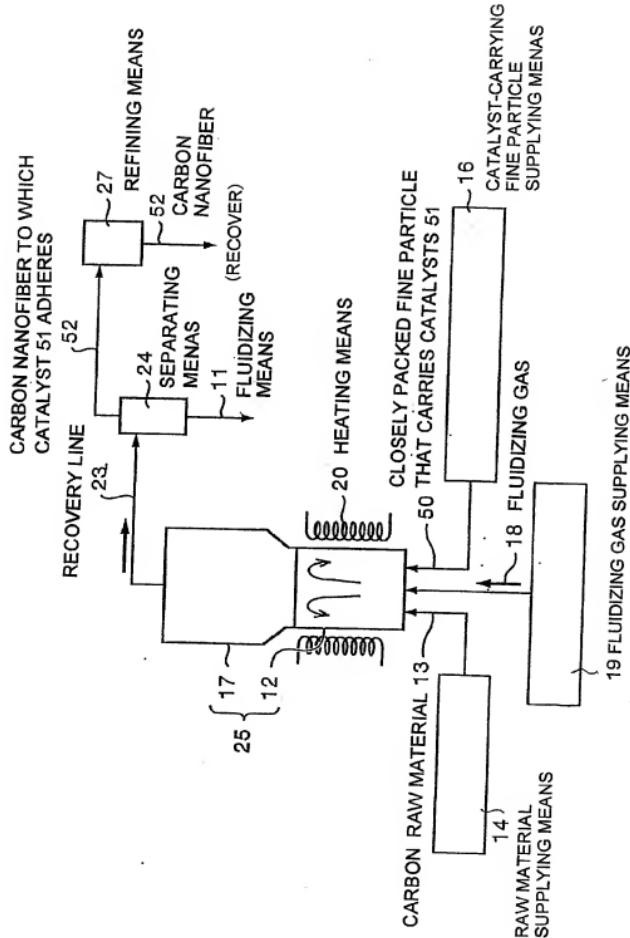


FIG. 14

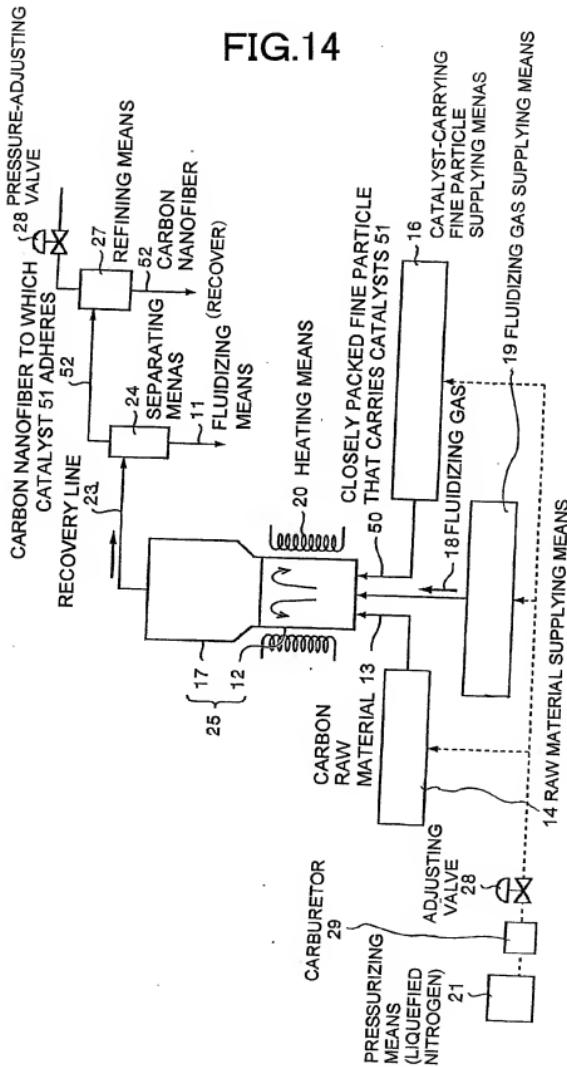


FIG.15

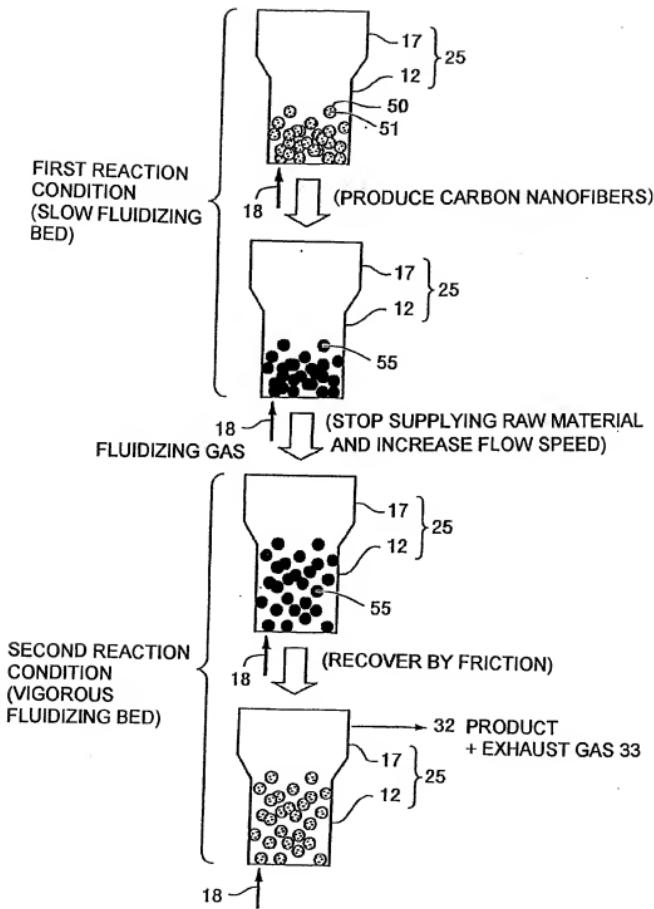


FIG.16

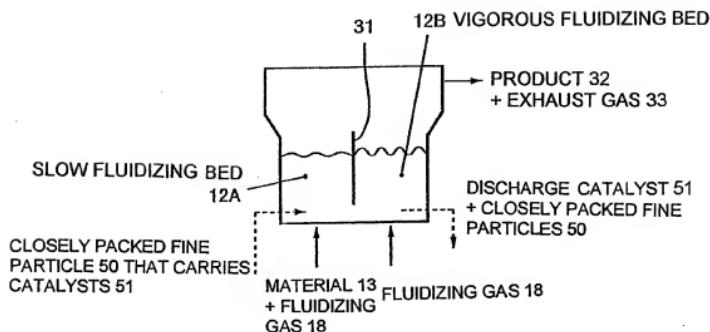


FIG.17

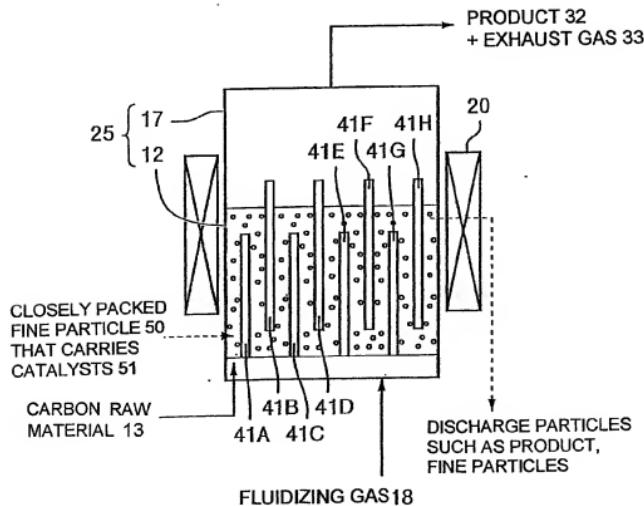
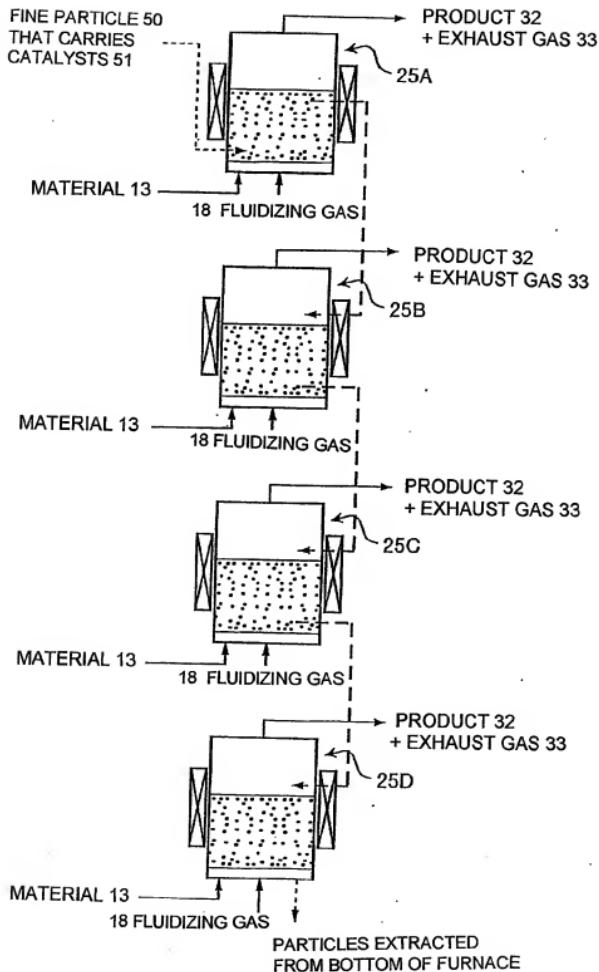
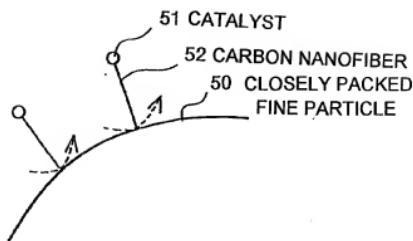


FIG. 18

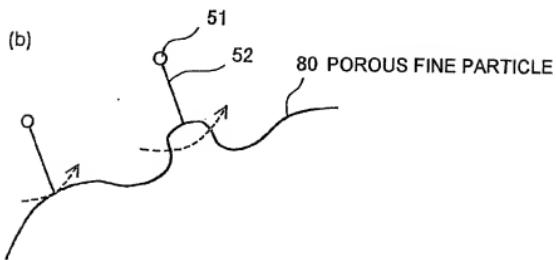


**FIG.19**

(a)



(b)



(c)

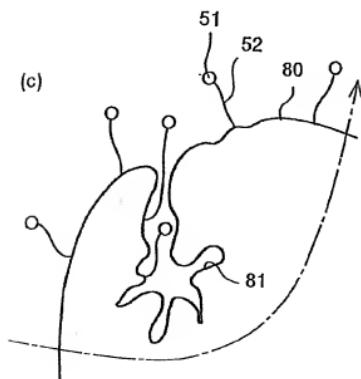


FIG.20

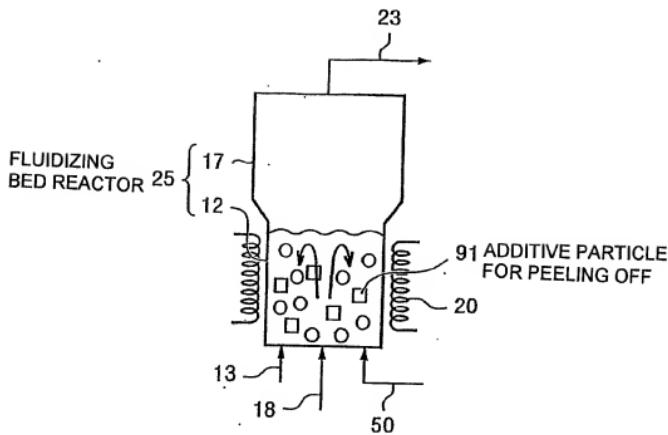


FIG.22

